N71-24198

NASA TT F-13,546

THERMODYNAMIC STUDY OF THE REACTION OF TUNGSTEN WIRES WITH OXYGEN AND CARBON DIOXIDES AT 1500 - 3500°K

H. Schafer

Translation of "Thermodynamische Untersuchung zur Reaktion von Wolframdrahten mit O_2 und CO_2 bei Temperaturen zwischen 1500 und 3500 °K"

In: Zeitschrift für Anorganische und Allgemeine Chemie,
Vol. 376, No. 1, 1970, pp. 11-27.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 APRIL 1971

Z. Anorg. Allg. Chem. 376, 11-27 (1970)

THERMODYNAMIC STUDY OF THE REACTION OF TUNGSTEN FILAMENTS WITH OXYGEN AND CARBON DIOXIDE AT 1500 - 3500° K (1)

by

Harald Schaefer

Based on experiments of R.J. Campbell (2), P. Wiedijk (3) and L. Bexten (4)

8 figures

ABSTRACT

A tungsten filament glows in an inert gas containing very small concentrations of oxygen ($N_2 + O_2$; $CO + CO_2$), at atmospheric pressure. Filament temperatures range from 1500 to 3500° K. The following observations are explained on the basis of thermodynamic equilibria existing at the surface of the filament and involving the species O_1, O_2, W_1, WO_2, WO_3, W_3O_9, W_4O_{12}:

- The inversion of the direction of tungsten transport in a temperature gradient at about 2800° K;
- the unusually sharp decrease in the amount of tungsten vaporized below 1600° K, and
- the order of magnitude of tungsten vaporization.

1. INTRODUCTION

During the reaction of incandescent filaments with gases at not too low total pressures (e.g., atmospheric pressure), thermodynamic equilibria are established at the filament surface. This has been demonstrated, for example, for the reaction of iridium, platinum and rhodium with oxygen (5). In this case, the gaseous oxides IrO_3, PtO_2 and RhO_2 are formed around 2000° K. A similar study has also been made (6) of the equilibrium $C + CS_2 = 2\ CS$ on incandescent carbon filaments (1500° C).

The following study which concerns the reaction of incandescent tungsten filament with oxygen - at low partial oxygen pressures, but with $\Sigma P = 1$ atm - is also based on the premise that the processes under investigation are largely dependent on thermodynamics.

2. EXPERIMENTAL BASE

2.1 Principle of the Iodine Lamp

During the last 10 years, iodine lamps (7,8) have gained considerable importance. These lamps contain an inert gas (e.g., argon at a pressure of 1 atm at room temperature), iodine and a small amount of oxygen. The tungsten vaporized off the incandescent filament reacts with the gaseous environment affording WO_2I_2. In contact with this filament, the latter is decomposed into the elements. In this manner, the tungsten removed by vaporization is replaced and a steady state is established.

For tungsten transport via gaseous WO_2I_2 the reader is also referred to ref (9).

According to Zubler and Mosby (10), the iodine pressure in a newly filled lamp amounts to a few, for example five, torr, and the oxygen pressure to 0.3 -0.5 torr. These values agree with those found by Philips (11).

Since the iodine does not participate in the processes occurring at the incandescent filament at about 3000° K and affords $WO_2I_{2,g}$ only at lower temperatures, (8,12), the tungsten - oxygen system is the only one affecting the filament.

In an operating lamp, the average temperature of the lamp filling may be assumed to be 1000° K. Hence, the oxygen pressure at the above-cited oxygen concentrations is about $2x10^{-3}$ atm.

2.2 The Experiments of Campbell (2)

This worker experimented with a cylindrical lamp containing a tungsten coil supported at a distance from the lamp wall by four tungsten wires. The conductive heat loss at the support sites caused a drop in temperature of the electrically heated coil. By allowing nitrogen containing known amounts of oxygen to pass through the lamp at atmospheric pressure, he observed visually a transport of tungsten owing to the temperature gradient between the turns of the coil which was heated to about 3000° K

The results of these experiments are shown in Table 1. The 3 - 510 ppm range of oxygen concentrations in the nitrogen carrier gas (1 atm) studied corresponds to oxygen pressures ranging from $3x10^{-6}$ to $5.1x10^{-4}$ atm.

Of particular significance is the observation that the direction of the tungsten transport in the temperature gradient of the coil is reversed when the oxygen pressure is increased.

2.3 The Experiments of Wiedijk (3)

These experiments were also carried out in open incandescent lamps under conditions of gas flow.

The pear-shaped lamp used (Philips GLS, 40 w, 220-230 v) contained a double tungsten coil having an outer diameter of approximately 0.4 mm. The free coil was about 24 mm long and weighed 5.3 mg. A stream of nitrogen containing 10, 20 and 40 ppm of O_2 was passed through the lamp with the temperature of the incandescent filament between 1473° and 2873° K. The weight loss of the tungsten coil, $\Delta_{wt.}$, was determined from the drop in current, ΔJ, since, for slight weight losses, $\Delta J/J = \Delta_{wt.}/\text{weight}$ (constant voltage).

The results are shown in Fig. 1. Noteworthy is the plateau of the curve indicating a maximum vaporization of tungsten between 1800° and 2400° K.

For an oxygen concentration of 40 ppm at 2390° K, $\Delta J/J = 0.027$ per hour which corresponds to a tungsten vaporization of 0.143 mg/hr. A comparison of this value with values obtained by thermodynamic calculations will follow (section 3.5).

2.4 The Experiments of Bexten (4)

At Muenster, the reaction of incandescent tungsten filaments in a CO_2/CO atmosphere was studied. The equilibrium oxygen pressures determined for the CO_2/CO gas phase were of similar magnitude as those resulting from the experiments described in sections 2.2 and 2.3.

Bexten did not use a tungsten coil, but an uncoiled filament having an actual length of 16.8 cm and a diameter of 0.03 cm. The filament connected two nickel terminals within a cylindrical horizontal glass jacket (35 cm long, 8 cm in diameter); it was heated by passing through it an electric current supplied from a stabilized source. The glass jacket was fitted with a glass bridge (tube diameter: 3 cm) sections of which were cooled or heated to cause convection and, hence, constant movement of gas through the reaction zone. The total volume of gas involved in the measurements was 2.6 liters.

All experiments were carried out at a filament temperature of 2730° K (corr.) over a period of 30 min. The gas pressure was 1 atm. The gaseous filler consisted of highly purified CO containing 0.2 - 1.4 vol.% of CO_2.

The gas was analyzed after each experiment (condensation of CO_2 and measurement of the gas volume). The small amount of CO_2 consumed in the reaction with tungsten was taken into account and the the CO_2 concentration corrected accordingly ("average CO_2 content of the gas phase").

The tungsten oxides formed on the filament deposited on the glass wall and no longer took part in the reaction.

Following the measurements, the filament gave an unchanged X-ray diagram of pure tungsten, but was found to be brittle. This suggested the presence of a small amount of absorbed carbon. According to thermodynamic calculations, under the prevailing experimental conditions, tungsten carbides are not stable as a separate phase. In fact, the formation of these carbides has thus far not been observed.

The weight loss of tungsten was determined by means of a micro balance. For a filament weighing 235 mg, this loss ranged from 0.1 to 10 mg.

The results of four series of measurements made at different times in slightly different apparatus are shown in Fig. 2.

2.5 Additional Observations

In other experiments, Campbell (2) and Wiedijk (3) used a nitrogen carrier gas containing defined amounts of I_2 and Br_2. These experiments will not be discussed here; however, they are amenable to a similar evaluation.

3. THERMODYNAMIC DISCUSSION

The gas phase existing under the conditions studied experimentally has a complex composition. It was deemed hopeless to try to determine this composition on the basis of the cited, rather simple experiments. A thermodynamic calculation of this composition followed by a comparison of the data with experimental values looked more promising. This is particularly true for unusual points, e.g., those exhibiting a change in the direction of transport of the filament material along the temperature gradient ("inversion points"). The following calculation exemplifies the treatment of such a multicomponent system involving the species O_1, O_2, CO, CO_2, W_1, WO_1, WO_2, WO_3, W_3O_9 and W_4O_{12}.

The following considerations refer to a model; hence, it is unimportant that some of the available thermodynamic data are uncertain (13). If, necessary, the numerical evaluation could be repeated in the future using more accurate data that may become avilable. Or, additional gas molecules (W_2O_6, W_3O_8 ?) could be considered without essentially changing the method of calculation.

3.1 Thermodynamic Data

The basic thermodynamicdata were taken from the Janaf tables (14). Table 2 shows these data, i.e., the values of log K_f for the formation of molecules from the elements in the standard state. For elements in the standard state, (O_2, W_f), by definition log K_f = zero at all temperatures. All pressures are given in atmospheres.

The calculations are based on equilibria /1/ through /9/

$$\begin{array}{llll}
0{,}5\,WO_{2,f} & = 0{,}5\,W_{,f} + O_1 & K_1 & (1) \\
WO_{2,f} & = W_{,f} + O_2 & K_2 & (2) \\
2\,O_1 & = O_2 & K_3 & (3) \\
W_{,f} + O_1 & = WO_{1,g} & K_4 & (4) \\
W_{,f} + 2\,O_1 & = WO_{2,g} & K_5 & (5) \\
W_{,f} + 3\,O_1 & = WO_{3,g} & K_6 & (6) \\
3\,W_{,f} + 9\,O_1 & = W_3O_{9,g} & K_7 & (7) \\
4\,W_{,f} + 12\,O_1 & = W_4O_{12,g} & K_8 & (8) \\
CO_2 & = CO + O_1 & K_9 & (9)
\end{array}$$

/1/ - /9/

By combining the formation constants ($\log K_f$) listed in Table 2, the values of the equilibrium constants K_1 through K_9 were obtained. These values are given in Table 3.

3.2 Maximum Concentration of Free Oxygen (O_2 and O_1) in the Gas Phase

Equilibria /1/ and /2/ limit the concentration of free oxygen in the gas phase

$$0{,}5\,WO_{2,f} = 0{,}5\,W_{,f} + O_1; \qquad K_1 \qquad /1/$$

$$WO_{2,f} = W_{,f} + O_2 \;; \qquad K_2 \qquad /2/$$

Since $K_1 = P(O_1)$ and $K_2 = P(O_2)$, the cited equilibrium constants (Table 3) indicate directly the pressures over $W_{,f} + WO_{2,f}$. Thus, preselected, higher oxygen pressures are reduced to equilibrium values with formation of solid WO_2.

A comparison of K_1 with O_1 pressures calculated for temperatures between 2000° and 3500° K (Figs. 3-6) shows that, in the considered pressure range, the formation of solid WO_2 does not take place. However, this is no longer true for lower temperatures (cf. section 3.5).

In conventional iodine lamps (section 2.1), the formation of WO_2 on the cooler tungsten surfaces (ends of the incandescent filament, tungsten supports for the coil) is prevented by the formation of $WO_2I_{2,g}$. Because of the thermal instability of WO_2I_2 in the hot region of the incandescent filament (~3000° K), the iodine concentration in the gas phase has no effect on the tungsten - oxygen equilibria in this region. This was confirmed by the experiments of Baxten involving the described incandescent filament method (4).

3.3 Equilibrium Pressures at Constant Temperature and Variation of $P(O_1)$

The partial pressures of O_2, WO_1, WO_2, WO_3, W_3O_9 and W_4O_{12} were calculated for the temperatures of 2000, 2200, 2500, 2800, 3000, 3200 and 3500° K and for wide ranges of predetermined $P(O_1)$ equilibrium pressures by means of a computer (IBM 360). The K values given in Table 3 were used for this purpose. In addition, the sums $\Sigma P(O_1)$ and $\Sigma P(W_1)$ were calculated.

$$\Sigma P(O_1) = P(O_1) + 2P(O_2) + P(WO_1) + 2P(WO_2) + 3P(WO_3) + 9P(W_3O_9) \qquad /10/$$

$$\Sigma P(W_1) = P(W_1) + P(WO_1) + P(WO_2) + P(WO_3) + 3P(W_3O_9). \qquad /11/$$

These sums do not include W_4O_{12} because of its negligible partial pressure.

$\Sigma P(O_1)$ is a measure of the initial oxygen pressure. In view of the observations made, the region for which $\Sigma P(O_1) = 10^{-6} - 10^{-3}$ atm is of interest. The equilibrium pressures for this region are shown in Figs. 3-6.

$\Sigma P(W_1)$ is a measure of the total tungsten concentration in the gas phase and, hence, of tungsten vaporization.

The following conclusions can be drawn from Figs. 3 - 6:

In the entire range studied, $P(O_1) \gg P(O_2)$.

At 2000° K, the total amount of oxygen introduced is fixed as W_3O_9 (more generally: $(WO_3)_n$); hence, $\Sigma P(W_1) \cong 1/3 \, \Sigma P(O_1)$.

At 2500° K, nearly all gaseous tungsten oxides must be considered. The situation is very complicated. (In this region, change in thermodynamic values would have a major effect on the individual pressures).

At 3000° K, W_1 predominates. The effect of higher oxides is slight.

At 3500° K, the determining factor is, besides WO_1, the tungsten saturation pressure $P(W_1)$. The other oxides can be neglected, $\Sigma P(W_1) = P(W_1) + P(WO_1)$. At low values of $\Sigma P(O_1)$, $\Sigma P(W_1)$ becomes the tungsten saturation pressure.

3.4 Inversion of the Direction of Tungsten Transport in the Temperature Gradient. Connection with the Observations of Campbell (2).

From the isotherms (Figs 3-6), the equilibrium pressures for any desired initial oxygen pressure $\Sigma P(O_1)$ can be obtained. However, only $\Sigma P(W_1)$ and its temperature dependence are essential for the tungsten transport and the comparison with Campbell's observations. For this reason, $\Sigma P(W_1)$ was obtained from Figs. 3-6 for all temperatures between 2000° and 3500° K and for $\Sigma P(O_1) = 10^{-5}$, 5×10^{-5}, 10^{-4} and 10^{-3} atm (and from subsequent figures for 2200°, 2800° and 3200° K) and is given in Table 4 and Fig. 7.

It is particularly important that, with increasing temperature, $\Sigma P(W_1)$ goes through a minimum. The absolute value of this minimum increases with increasing $\Sigma P(O_1)$ (Fig. 7, which represents a logarithmic plot gives the opposite impression).

In addition, with increasing $\Sigma P(O_1)$, the minimum is shifted toward the higher temperatures.

The appearance of the minimum is connected with the fact that, at lower temperatures, $\Sigma P(W_1)$ is determined primarily by the exothermic formation of W_3O_9, WO_3 and WO_2, whereas at higher temperatures it is determined by the endothermic formation of WO_1 and W_1. The temperature dependence of the equilibria is shown also in Table 3.

The minimum means that, in a temperature gradient - depending on experimental conditions - tungsten can not only be transported to regions of lower temperature but also to regions of higher temperature. Since tungsten always migrates to the region with the lower value of $\Sigma P(W_1)$, it is possible to select on the curves of Fig. 7 any two temperatures and indicate for that particular case the direction of tungsten transport.

The inversion of the transport direction in a temperature gradient has previously been reported for other systems (15).

Campbell realized (2) that the interaction of the exothermic formation of WO_2 and the endothermic formation of WO_1 is important for the directional dependence of tungsten transport on the temperature and oxygen content of the carrier gas observed by him. Our current calculations confirm this qualitative conclusion and place it on a quantitative basis. The nitrogen carrier gas in Campbell's experiments was at atmospheric pressure. Hence, 1 ppm of oxygen corresponds to an oxygen pressure of 1×10^{-6} atm. The initial O_1 pressure is then $\Sigma P(O_1) = 2 \times 10^{-6}$ atm. The pressures calculated in this manner and the observed transport directions (Table 1) can be summarized as follows ($T_1 < 2800°$ K; $T_2 > 2800°$ K):

Experiment B:	$\Sigma P(O_1) = 6\times10^{-6}$ atm,	W transport	$2800° \leftarrow 3000°$ K
C	1.1×10^{-4}		$2500 \rightarrow 3000$
D	1.1×10^{-4}		$T_1 \rightarrow 2800 \leftarrow T_2$
E	1.0×10^{-3}		$2800 \rightarrow 3000$

These experimental results are shown in Fig. 7. The experimental transport directions are in full agreement with the calculated curves. In other words, the thermodynamic model adequately describes the phenomena observed.

From this it follows that our calculations provide a useful basis also for further considerations, for example, of the phenomena taking place in special incandescent lamps.

3.5 Transition to Temperatures Below 2000° K. Connection with the Observations of Wiedijk.

At lower temperatures, the $\Sigma P(W_1) - T$ curves (Fig. 7) become horizontal. This is due to the fact that, under these conditions, nearly all of the oxygen introduced is bound as $W_3O_{9,g}$. Thus, $\Sigma P(W_1) = 3 \cdot P(W_3O_9) = 3/9\ \Sigma P(O_1)$ becomes an upper limiting value. This value is nearly attained at 2000° K. At lower temperatures, the plot reaches the value of the W_3O_9 pressure over the heterogeneous solid phase $W + WO_{2,f}$, eq. /12/

$$9\,WO_{2,f} = 3\,W_{,f} + 2\,W_3O_{9,g}. \qquad /12/$$

Table 5 shows the W_3O_9 pressures for equilibrium /12/ calculated from the values of the formation constant K_f of the reactants (14). These values as well as $\Sigma P(W_1)$ (for $\Sigma P(O_1) = 10^{-4}$ atm) are shown as a function of temperature in Fig. 8.

It can be seen from Fig. 8 that the tungsten content of the gas phase $\Sigma P(W_1)$ at the cited oxygen concentrations $\Sigma P(O_1)$ in the gas stream introduced varies in a complicated manner. With increasing temperature, the following curve segments can be distinguished (Fig. 8):

a) A sharp increase of $\Sigma P(W_1)$ over $W_{,f} + WO_{2,f}$ as the solid phase

b) "W_3O_9 plateau"; prevalent binding of oxygen as W_3O_9;

c) Exothermic decrease owing to equilibria involving the prevalent formation WO_2, WO_3 and W_3O_9 as the gaseous species;

d) Minimum resulting from the mutual compensation of exothermic and endothermic processes;

e) Endothermic increase owing to the predominant formation of WO_1 and W_1 species.

Segments a, b and c of the curve explain the flat maximum observed by Wiedijk (section 2.3, Fig.1). This worker used, for example, a gas stream containing 40 ppm of oxygen which corresponds to a $\Sigma P(O_1)$ of 0.8×10^{-4} atm. which is in good agreement with Fig. 8. Wiedijk's experimental point at 1473° K falls on the ascending segment a, the points for 1773° and 2400° K fall on plateau b and the points for 2610°, 2773° and 2873° K on the exothermic segment c.

Wiedijk determined the vaporization of tungsten by measuring the change in current $\Delta J/J$. Along segment a, no well defined relationship exists between this change and $\Sigma P(W_1)$. The quantity $\Delta J/J$ reflects a decrease in the amount of elemental tungsten in an approximate manner and regardless of whether the tungsten is transferred to the gaseous phase as an oxide or whether solid WO_2 is deposited. Hence, "segment "a" in Wiedijk's experiments must be interpreted as meaning that a layer of WO_2 prevents further reaction.

This provides a qualitative explanation of the experimental curve (Fig. 1). The quantitative aspects can be summarized as follows. The plausible assumption is made that the double tungsten coil can be treated as a single filament with equilibrium pressures established at its surface. Material transport occurs by diffusion through the Langmuir layer. Based on considerations developed in the following section and using the quantities

$\Sigma P(O_1) = 8 \times 10^{-5}$ atm, $\Sigma P(W_1) = 2 \times 10^{-5}$ atm (according to Fig. 7), $T = 2390°$ K, radius of the Langmuir layer: $r_2 = 0.25$ cm, filament radius $r_1 = 0.02$ cm, filament length $l = 2.4$ cm, diffusion coefficient within the Langmuir layer $D = 2.5$ cm^2 sec^{-1}. The tungsten vaporization was calculated to be 1.0 mg of W/hr. Wiedijk's experiment gave a value of 0.143 mg of W/hr (section 2.3). Considering the computational and experimental sources of error, only an agreement in order of magnitude was to be expected.

3.6 Reaction of Tungsten in a CO_2/CO Atmosphere. Connection with the Experiments of Bexten.

Fig. 2 shows the amount of tungsten vaporized off an incandescent filament (2730° K) by the action of CO_2/CO.

Knowledge of the partial pressures prevailing at the incandescent filament permits the estimation of vaporized tungsten and comparison with experimental data.

EQUILIBRIUM PRESSURES AT THE INCANDESCENT FILAMENT. Since a certain oxygen pressure is associated with the previously cited CO_2/CO mixture, the following calculation is based on the equilibrium pressures calculated in section 3.3: From $P(O_1)$, $P(CO) = 1$ atm and K_9, the value of the equilibrium pressure $P(CO_2)$ was calculated. From the latter value, the corresponding initial CO_2 pressure $\Sigma P(CO_2) = P(CO_2) + \Sigma P(O_1)$ was obtained. This pressure is given as an example on top of Fig. 4. Otherwise the CO_2 consumption during the reaction is small, $\Sigma P(O_1) \ll \Sigma P(CO_2)$.

At the temperature of the experiment (2730° C)(sic) K, for the examined range of partial pressures at the incandescent filament, $P(WO1) \gg P(WO_2) > P(WO_3) \gg P(W_3O_9)$ and

$P(CO_2) \gg P(O_1) \gg P(O_2)$.

THE LANGMUIR LAYER. An incandescent filament in a (cooler) gas atmosphere causes thermal convection in the latter. However, this convection stream does not affect a cylindrical gas layer in the immediate vicinity of the filament. Molecules can penetrate this "Langmuir layer" (16) only by diffusion. The composition at the outer boundary of the Langmuir layer corresponds to that of the external gas mass streaming by as a result of convection. The composition at the inner boundary of the Langmuir layer, i.e., at the filament - gas interface, is determined by the reaction between the gas and the filament.

The radius of the Langmuir layer, r_2, for the filament radius in Bexten's experiment ($r_1 = 0.015$ cm) was estimated at 0.25 cm with the aid of Langmuir's data (16). The processes in the Langmuir layer are complicated. We must be content with an approximate calculation. Pertinent considerations are as follows.

The temperature in the Langmuir layer decreases from that at the incandescent filament to essentially room temperature. The variations in temperature and the temperature dependence of the diffusion coefficients are not well known. One reason for this is the multiplicity of the chemical processes involved.

When WO_x molecules move from the incandescent filament into regions of lower temperature, chemical changes are to be expected;

$$WO_1 + CO_2 = WO_2 + CO \qquad /13/$$

$$WO_2 + CO_2 = WO_3 + CO \qquad /14/$$

$$3\,WO_3 = W_3O_9 \qquad /15/$$

Oxidation and aggregation processes take place; cf/ equations /13/-/15/. If one neglects the differences between individual diffusion coefficients and if these reactions are reversible and rapid, then a concentration gradient for the total tungsten content ΣW_1 can be defined without these chemical processe affecting the calculation of the diffusion. That this concept approximates the real state of affairs is supported by Bexten's observation that iodine has no appreciable effect on the reaction of the CO_2/CO gas phase with tungsten (2730°K) although it is known that iodine "at intermediate temperatures" reacts with WO_x molecules affording $WO_2I_{2;g}$. The tungsten concentration of the gas phase defined in the above sense is not affected by the addition of iodine.

This iodine experiment is important also in another respect. When tungsten oxide molecules reach the cooler zones, nucleation and deposition of oxide clusters can eventually take place. Apparently, this effect also does not play a major role. The addition of iodine will repress it or shift it to substantially lower temperatures (deposition of WO_2I_2).

In view of the above situation, a calculation based on individual diffusion coefficients for the molecules involved would not make much sense. We used the average value $D_o = 0.1$ cm^2 sec^{-1} estimated for 273° K and 1 atm of CO pressure. The strong temperature dependence of the diffusion coefficients is described by the semi-empirical relationship /16/

$$D = D_0 \left(\frac{T}{273}\right)^{1,8}; \quad \Sigma P = 1 \text{ atm} \qquad /16/$$

By averaging the D values for gradually increasing temperatures between 500° and 3000° K, the average value within the Langmuir layer was found to be $D = 3.3$ cm^2 sec^{-1}.

Thermal diffusion and the attendant enrichment in heavy molecules at lower temperatures will not be discussed here.

The following symbols are used in the calculation of the diffusion:

n = diffusing molecules

D = diffusion coefficient, cm^2 sec^{-1}

r = diffusion path, cm

r_1 = filament radius, cm

r_2 = radius of Langmuir layer, cm

l = filament length, cm

t = duration of experiment, sec

c_1 = concentration at the filament surface, mole cm^{-3}

c_2 = concentration at the outer boundary of the Langmuir layer, mole cm^{-3}

P_1 = partial pressure at the filament surface, atm

R = 82, cm^3 atm $degree^{-1}$ $mole^{-1}$

T_1 = temperature, at the filament surface, °K

Eq. /17/ is valid for the steady state in which the same number of molecules diffuses through each cylindrical surface area $2r\pi l$, where $r_1 < r < r_2$.

$$n = -D \cdot 2\pi r \cdot l \cdot t \cdot \frac{dc}{dr}$$

$$\int_{c_2}^{c_1} dc = -\frac{n}{t} \cdot \frac{1}{2\pi \cdot l \cdot D} \cdot \int_{r_2}^{r_1} \frac{dr}{r} . \qquad /17/$$

Assuming diffusion of tungsten-containing molecules away from the filament and a tungsten-free external gas phase, then $c_2 = 0$, and hence:

$$c_1 = +\frac{n}{t} \cdot \frac{1}{2\pi l \cdot D} \cdot \ln\left(\frac{r_2}{r_1}\right)$$

or

$$n = \frac{c_1 \cdot t \cdot 2\pi l \cdot D}{\ln\left(\frac{r_2}{r_1}\right)} .$$

Considering that $c_1 = P_1/RT_1$, the above relation can be expressed in terms of pressures

$$n = \frac{P_1 \cdot t \cdot 2\pi l \cdot D}{R \cdot T_1 \cdot \ln\left(\frac{r_2}{r_1}\right)} .$$

CONNECTION WITH THE EXPERIMENT. For a CO gas phase containing 0.5 volumes of CO_2, $\Sigma P(CO_2) = 5 \times 10^{-3}$ atm. At thermodynamic equilibrium at 2800° K, the total tungsten concentration at the tungsten filament is then $\Sigma P(W_1) = P_1 = 3.4 \times 10^{-6}$ atm. The other parameters used in the calculation are: $t = 30.60$ sec, $l = 16.8$ cm, $D = 3.3\ cm^2\ sec^{-1}$, $T_1 = 2800°$ K, $r_2 = 0.25$ cm and $r_1 = 0.015$ cm.

The amount of tungsten vaporized in 30 min is then $n = 3.3 \times 10^{-6}$ gram-atoms or 0.6 mg of W. For 2750° K (instead of 2800° K) this value would be reduced to about 0.3 mg W/30 min.

However, Bexten's measurements gave a value of about 1.4 mg W/30 min (at 2730° K) This means that the calculated value is five times smaller than the experimental one.

Possible reasons for this are:

- the marked uncertainties of the initial thermodynamic data ;
- rough approximations in the estimation of the diffusion in the Langmuir layer as well as the extent of the experimental error.

It is noteworthy that Wiedijk's experimental values are lower than the calculated ones, whereas the opposite is true for Bexten's measurements.

An indication of systematic experimental error is found in the fact that the isothermal tungsten vaporization depends more strongly on the CO_2 content of the gas phase than would be expected on the basis of the equilibrium pressures.

If one takes into accouunt these numerous sources of error, the agreement between calculation and experiment may be considered as satisfactory.

4. CONCLUSIONS

This study proves that it is reasonable to subject the reaction of gases ($\Sigma P \sim 1$ atm !) with an incandescent tungsten filament to thermodynamic treatment. The model accounts for all phenomena observed. The results obtained with the still relatively simple W/O system encourage one to study systems such as W/O/H or W/O/X (X = halogen).

The author is indebted to the following colleagues: to Dr. E.G. Zubler and

Dr. R.J. Campbell for the use of the manuscript of their paper before publication; to Mr. P. Wiedijk for the use of unpublished experimental results; to Dr.L. Bexten for experimental cooperation and to Prof. Dr. E. Rabenau, Dr. L.M. Nijland, J.H. Dettingmeijer and Dr. J. Tillack for fruitful discussions.

Department of Inorganic Chemistry
University of Muenster

Received by the editor on December 3, 1969.

Address of the author: Prof. Dr. H. Schaefer
Anorganisch-Chemisches Institut der Universitaet Muenster
44 Muenster, Gievenbeckerweg 9

BIBLIOGRAPHY

(1) Preliminary communication: Z. Anorg. Allg. Chem. 373, 305 (1970).

(2) R.J. Campbell, J. High Temp. Sci 1, 303 (1969).

(3) P. Wiedijk, Philips, Eindhoven, private communication

(4) L. Bexten, "diploma" thesis, Muenster, 1967; additional measurements made during the preparation of the doctoral thesis.

(5) H. Schaefer and H.J. Heitland, Z. Anorg. Allg. Chem. 304, 249, 262 (1960).

(6) H. Schaefer and H. Wiedemeier, Ibid. 296, 241 (1958).

(7) E.G. Zubler and F.A. Mosby, Illumination Eng. 54, 734 (1959).

(8) A. Rabenau, Angew. Chem. 79, 43 (1967).

(9) J.H. Dettingmeijer, J. Tillack and H. Schaefer, Z. Anorg. Allg. Chem. 369, 161 (1969).

(10) E.G. Zubler and F.A. Mosby, U.S. Patent 3,160,454 (1964).

(11) For this communication, the author is indebted to Philips, Eindhoven.

(12) H. Schaefer, unpublished thermodynamic studies (1965).

(13) For $nWO_3,g = (WO_3)_{n,g}$, the association energies for $n = 2-4$ are reported with an uncertainty of ±20-30 kcal; cf. J. Drowart and P. Goldfinger, Angew. Chem. 79, 589 (1967).

(14) Janaf Thermochemical Tables, The Dow Chemical Co., Midland, Michigan (1961-63).

(15) H. Schaefer, "Chemische Transportreaktionen" (Chemical Transport Reactions), Weinheim, 1962, New York, London, 1964, Moscow, 1964.

(16) J. Langmuir, Phys. Rev. 34, 401 (1912); J. Amer. Chem. Soc. 34, 860 (1912).

TABLE 1

Tungsten Transport

Experiments of Campbell (2). N_2 carrier gas (1 atm) containing small amounts of oxygen. Temperatures are given in degrees K. The arrow indicates the direction of transport. $T_1 < 2800°$ K; $T_2 > 2800°$ K.

Experiment	O_2 content of the gas in ppm	Duration of experiment, hrs	Transport direction
A	<1	80	no transport at 2000-3050°
B	3	?	2800 <- 3000°
C	55	6	2500 -> 3000°
D	55	?	T_1 -> 2800° <- T_2
E	510	?	2800 -> 3000°

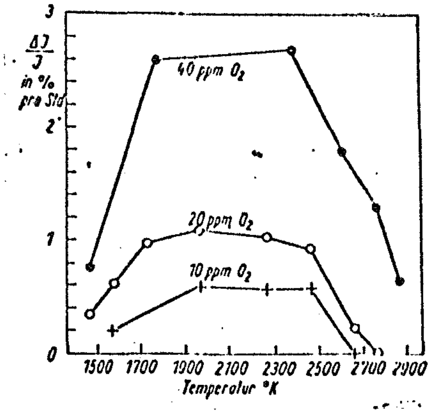

Fig. 1 - Experiments of Wiedijk (3). Current drop $\Delta J/J$ as a function of temperature.

The oxygen content of the N_2 carrier gas is as indicated.

Abscissa: temperature, °K ; ordinate: $\Delta J/J$, % per hour

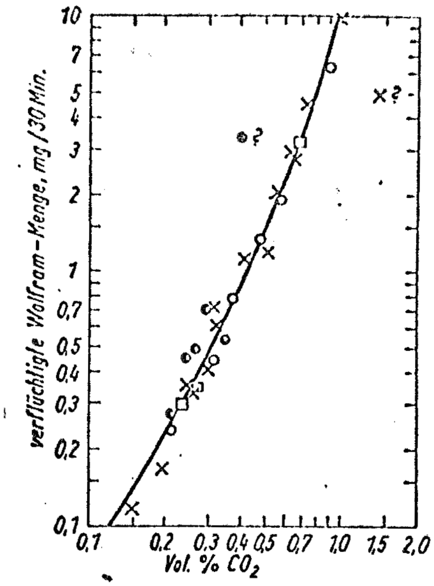

Fig. 2 - Reaction of a CO_2/CO phase ($\leq P = 1$ atm) with a tungsten filament heated at 2730° K. Data from 4 sets of measurements (4).

Abscissa: vol.% CO_2 ; ordinate: amount of tungsten vaporized, mg/30 min.

Table 2

TABLE 2

Values of log K_f for the formation of molecules from the elements in the reference state (14). The values in parentheses for $WO_{2,f}$ were obtained by graphic extrapolation.

Compound	Temperature, °K						
	2000	2200	2500	2800	3000	3200	3500
O_1	− 3,178	− 2,571	− 1,842	− 1,208	− 0,940	− 0,670	− 0,310
W_1	−14,433	−12,398	− 9,956	− 8,030	− 6,074	− 6,043	− 4,848
$WO_{1,g}$	− 5,554	− 4,540	− 3,352	− 2,420	− 1,907	− 1,462	− 0,805
$WO_{2,g}$	− 0,643	− 0,466	− 0,261	− 0,109	− 0,020	+ 0,038	+ 0,118
$WO_{2,f}$	+ 6,284	+ 4,961	+ 3,393	+ 2,182	+ 1,520	(+ 0,95)	(+ 0,20)
$WO_{3,g}$	+ 4,851	+ 4,150	+ 3,305	+ 2,630	+ 2,201	+ 1,931	+ 1,503
$W_3O_{9,g}$	+28,248	+23,728	+18,318	+14,072	+11,716	+ 9,654	+ 7,003
$W_4O_{12,g}$	+37,678	+31,341	+23,877	+18,024	+14,777	+11,937	+ 8,288
CO	+ 7,460	+ 7,185	+ 6,840	+ 6,503			
CO_2	+10,353	+ 9,411	+ 8,280	+ 7,388			

TABLE 3

Equilibrium constants (pressures in atm)

$P(W_1)$ is the saturation pressures over solid tungsten. The number following the slash is the exponent over base 10. For example, 4.786-7 means also 4.786×10^{-7}.

	2000°K	2200°K	2500°K	2800°K	3000°K	3200°K	3500°K
K_1	4,786/−7	8,882/−6	2,891/−4	4,375/−3	1,951/−2	7,162/−2	3,890/−1
K_2	5,200/−7	1,094/−5	4,046/−4	6,577/−3	3,020/−2	1,122/−1	6,310/−1
K_3	2,270/6	1,387/5	4,831/3	3,436/2	7,907/1	2,188/1	4,160
K_4	4,207/−3	1,052/−2	3,090/−2	7,047/−2	1,102/−1	1,614/−1	2,600/−1
K_5	5,164/5	4,742/4	2,640/3	2,673/2	7,396/1	2,383/1	5,470
K_6	2,427/14	7,295/11	6,776/8	2,754/6	1,282/5	8,730/3	2,710/2
K_7	7,080/56	7,362/46	7,871/31	3,048/25	1,807/20	4,831/15	6,209/9
K_8	5,176/75	1,560/62	9,572/45	1,738/33	1,462/26	9,451/19	1,010/12
K_9	8,670/−7	1,596/−5	5,224/−4	8,072/−3			
$P(W_1)$	3,690/−15	3,999/−13	1,107/−10	9,141/−9	1,062/−7	9,057/−7	1,419/−5

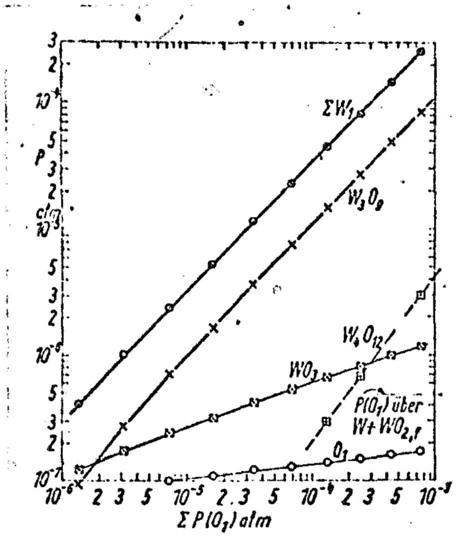

Figure 3

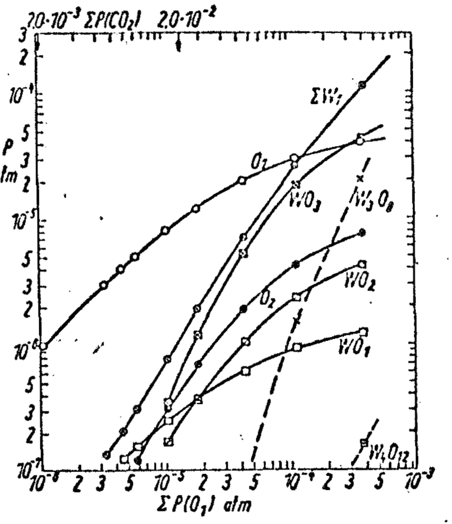

Figure 4

Fig. 3 - Equilibrium pressures over tungsten calculated for 2000°K. Here (as in all following figures), the experimental points are also given.

Key: 1 = $P(O_1)$ over $W + WO_{2,f}$

Fig. 4 - Equilibrium pressures over tungsten calculated for 2500° K

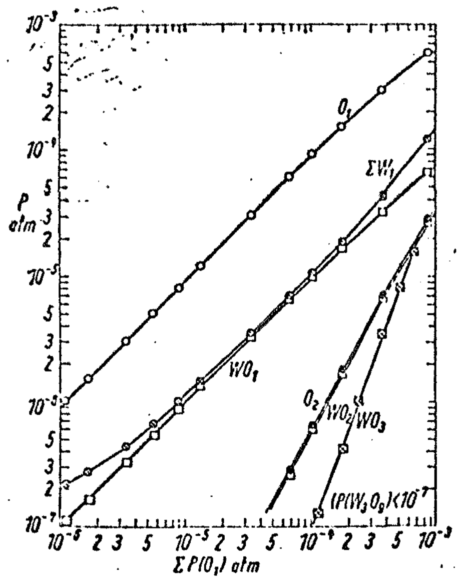

Figure 5

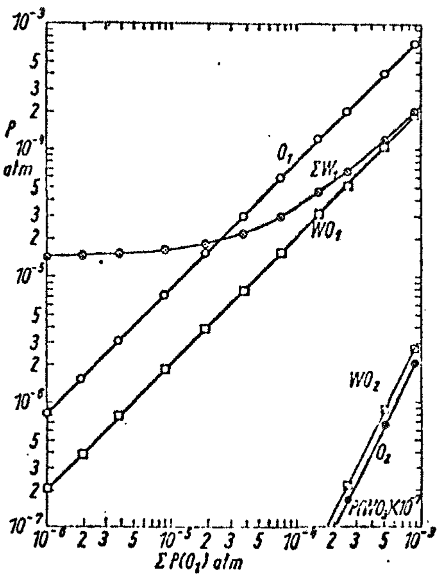

Figure 6

Fig. 5 - Equilibrium pressures over tungsten calculated for 3000° K.

Fig. 6 - Equilibrium pressures over tungsten calculated for 3500° K.

TABLE 4

Values of $P(W_1)$ in atm as a function of temperature and initial oxygen pressure $\Sigma P(O_1)$.

T °K	$\Sigma P(O_1)$			
	$1 \cdot 10^{-5}$ atm	$5 \cdot 10^{-5}$ atm	$1 \cdot 10^{-4}$ atm	$1 \cdot 10^{-3}$ atm
2000	$3{,}2 \cdot 10^{-6}$	$1{,}7 \cdot 10^{-5}$	$3{,}3 \cdot 10^{-5}$	$3{,}3 \cdot 10^{-4}$
2200	$2{,}8 \cdot 10^{-6}$	$1{,}6 \cdot 10^{-5}$	$3{,}2 \cdot 10^{-5}$	$3{,}3 \cdot 10^{-4}$
2500	$7{,}2 \cdot 10^{-7}$	$8{,}8 \cdot 10^{-6}$	$2{,}2 \cdot 10^{-5}$	$2{,}9 \cdot 10^{-4}$
2800	$6{,}8 \cdot 10^{-7}$	$3{,}9 \cdot 10^{-6}$	$9{,}0 \cdot 10^{-6}$	$2{,}1 \cdot 10^{-4}$
3000	$1{,}1 \cdot 10^{-6}$	$5{,}2 \cdot 10^{-6}$	$1{,}0 \cdot 10^{-5}$	$1{,}45 \cdot 10^{-4}$
3200	$2{,}3 \cdot 10^{-6}$	$8{,}0 \cdot 10^{-6}$	$1{,}5 \cdot 10^{-5}$	$1{,}5 \cdot 10^{-4}$
3500	$1{,}6 \cdot 10^{-5}$	$2{,}5 \cdot 10^{-5}$	$3{,}5 \cdot 10^{-5}$	$2{,}2 \cdot 10^{-4}$

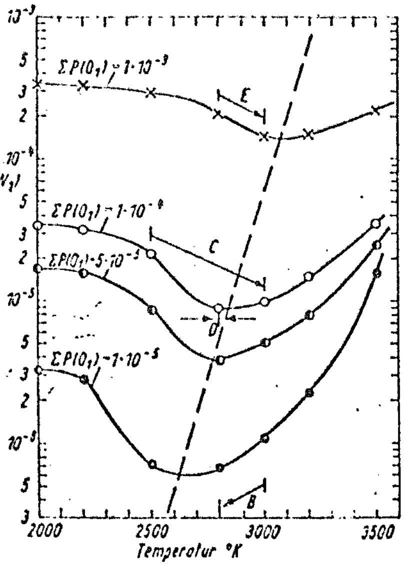

Fig. 7 - Plot of $\Sigma P(W_1)$ as a function of temperature for $\Sigma P(O_1) = 10^{-5}$, 5×10^{-5}, 10^{-4} and 10^{-3} atm. The letters B, C, D, E, indicate the experiments of Campbell (2). The direction of the tungsten transport observed is indicated by an arrow.

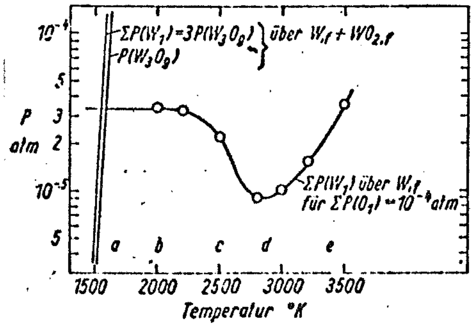

Fig. 8 - $\Sigma P(W_1)$ over $W_{,f} + WO_{2,f}$ and over $W_{,f}$ for $\Sigma P(O_1) = 10^{-4}$ atm as a function of temperature.

Key: 1 = $\Sigma P(W_1)$ over $W_{,f}$ for $\Sigma P(O_1) = 10^{-4}$ atm; 2 = over $W_{,f} + WO_{2,f}$

TABLE 5

W_3O_9 pressures over $W_{,f} + WO_{2,f}$
K_f are the formation constants of the compounds (14)

T °K	log K_f ($WO_{2,f}$)	log K_f ($W_3O_{9,g}$)	P(W_3O_9)
1400	12,642	49,656	$5{,}85 \cdot 10^{-8}$
1500	11,217	44,885	$2{,}56 \cdot 10^{-6}$
1600	9,975	40,716	$6{,}74 \cdot 10^{-5}$
1700	8,883	37,041	$1{,}17 \cdot 10^{-3}$

Translated for the National Aeronautics and Space Administration by Scripta Technica, Inc. NASW 2036